

## Introduction & scope

**Esterification & Transesterification reactions** play a key role in today's **biorefineries**. Conventionally, these reactions are performed using an acid or a base **homogeneous catalyst**.

### Heterogeneous catalysis

- (+) not dedicated catalyst separation
- (+) no purification.

**acid ion-exchange resin** can catalyze

- (+) ecofriendly
- (+) non corrosive
- (+) good stability
- (+) reusability

(!) swelling in a polar solvent => determines the **accessibility** of its active sites  
=> critical role in **reaction kinetics**

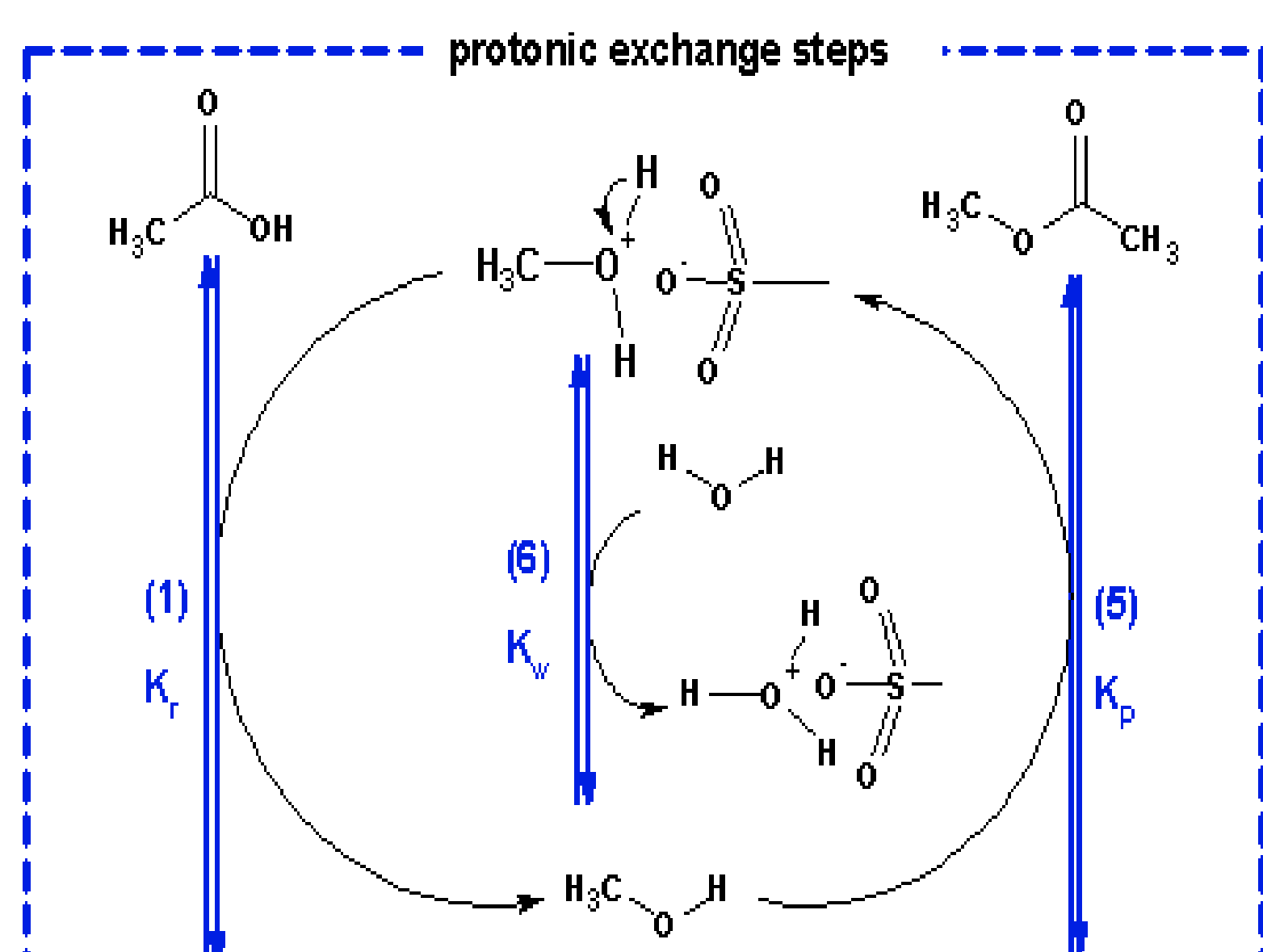
esterification

transesterification

## Esterification

## Transesterification

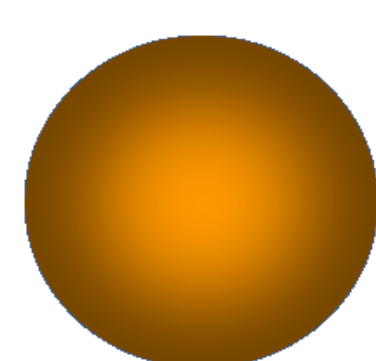
## Reaction Mechanism & Kinetic model



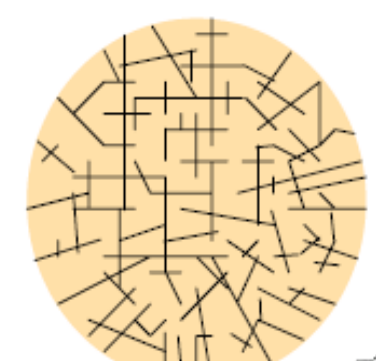
$$r = \frac{k_{SR} K_r \left( a_{AcAc} - \frac{1}{K_{eq}} \frac{a_{MeOAc} a_{H_2O}}{a_{MeOH}} \right)}{1 + K_r \frac{a_{AcAc}}{a_{MeOH}} + K_p \frac{a_{MeOAc}}{a_{MeOH}} + K_w \frac{a_{H_2O}}{a_{MeOH}}}$$

### Catalyst

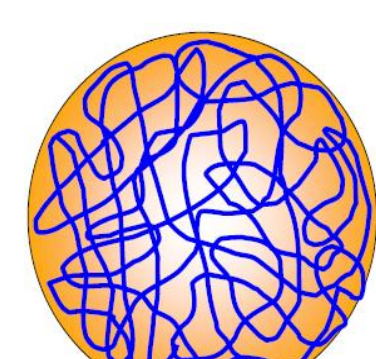
Lewatit K1221



✓ No permanent pore structure

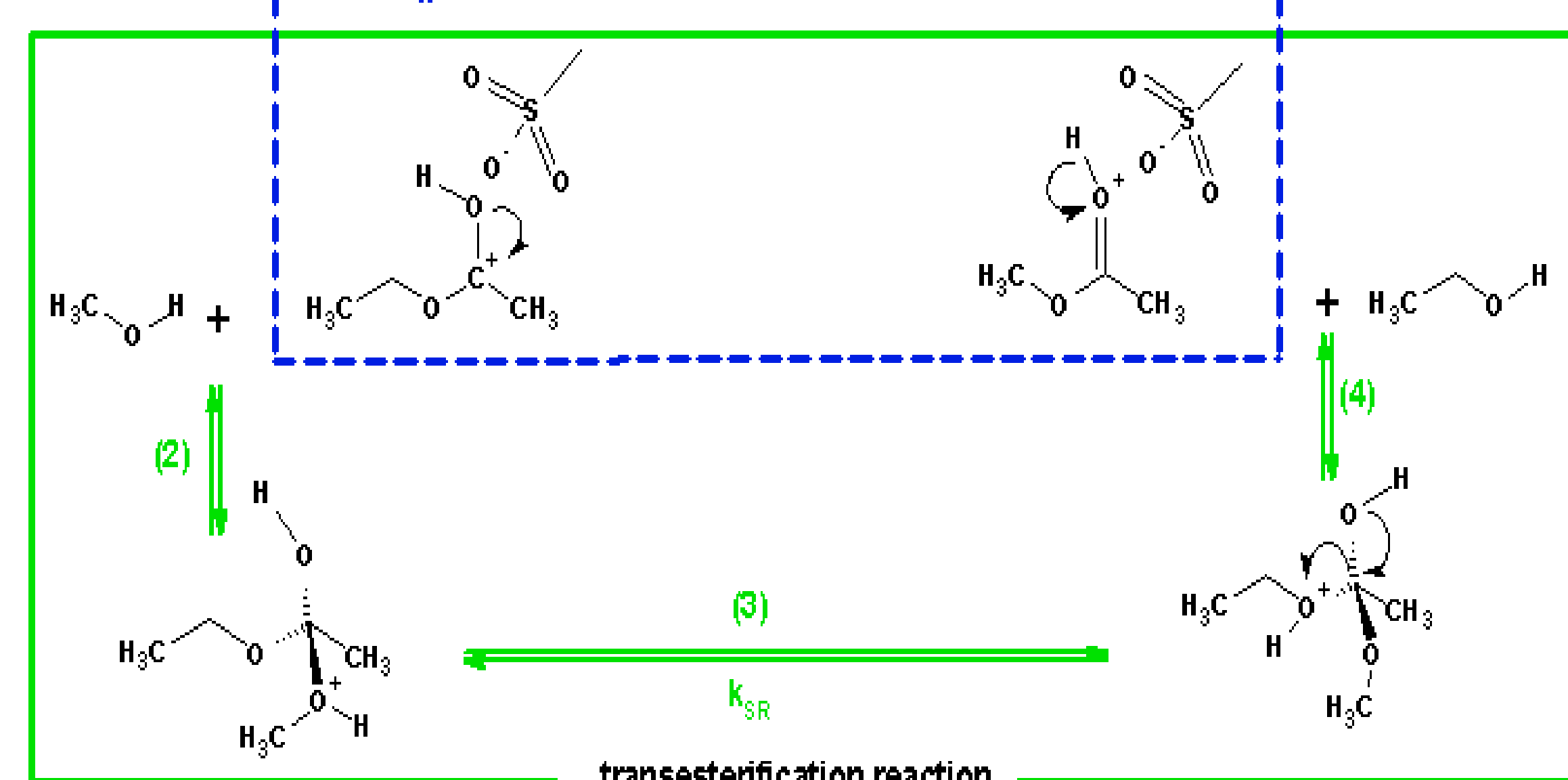
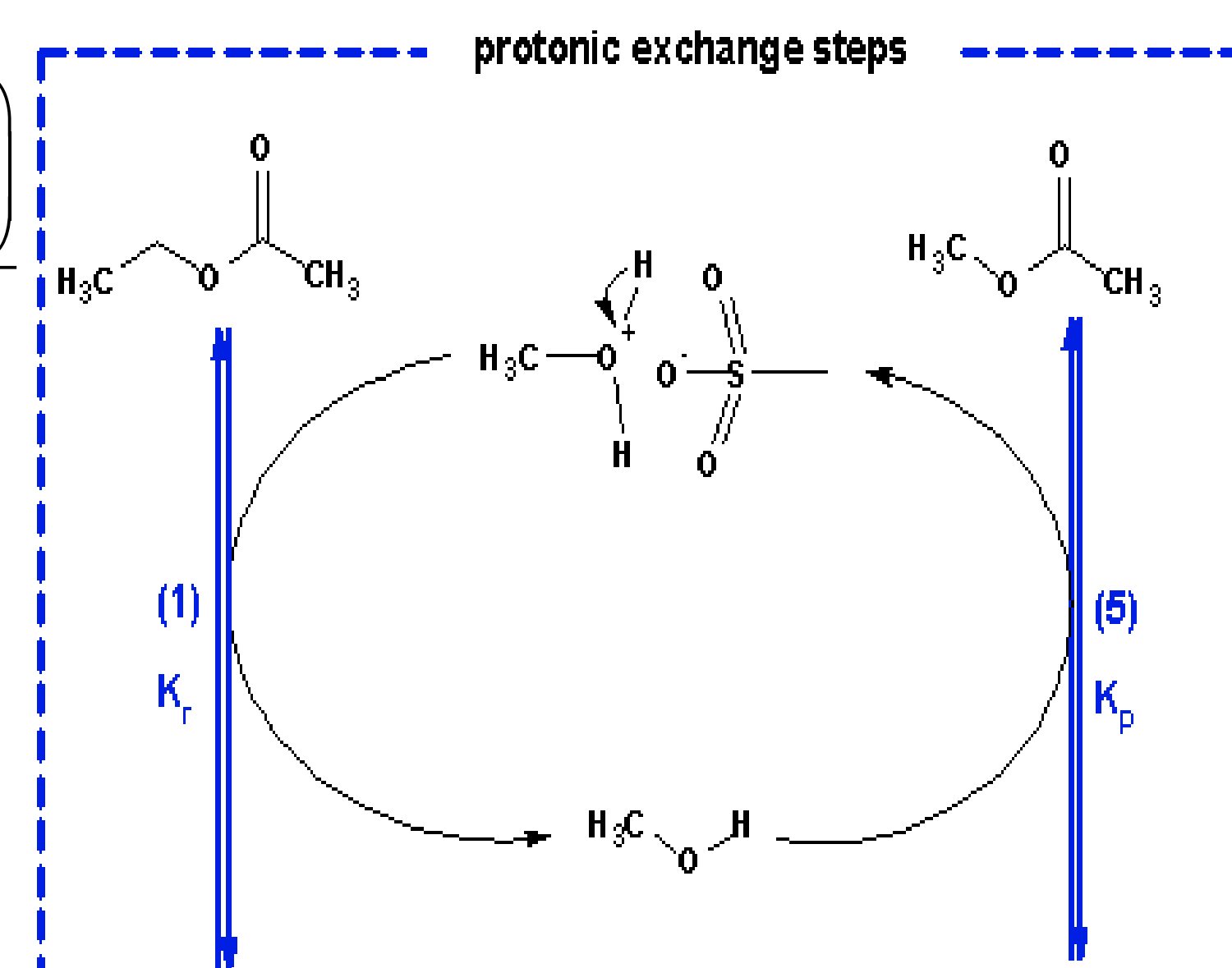


✓ Pore structure obtained by swelling

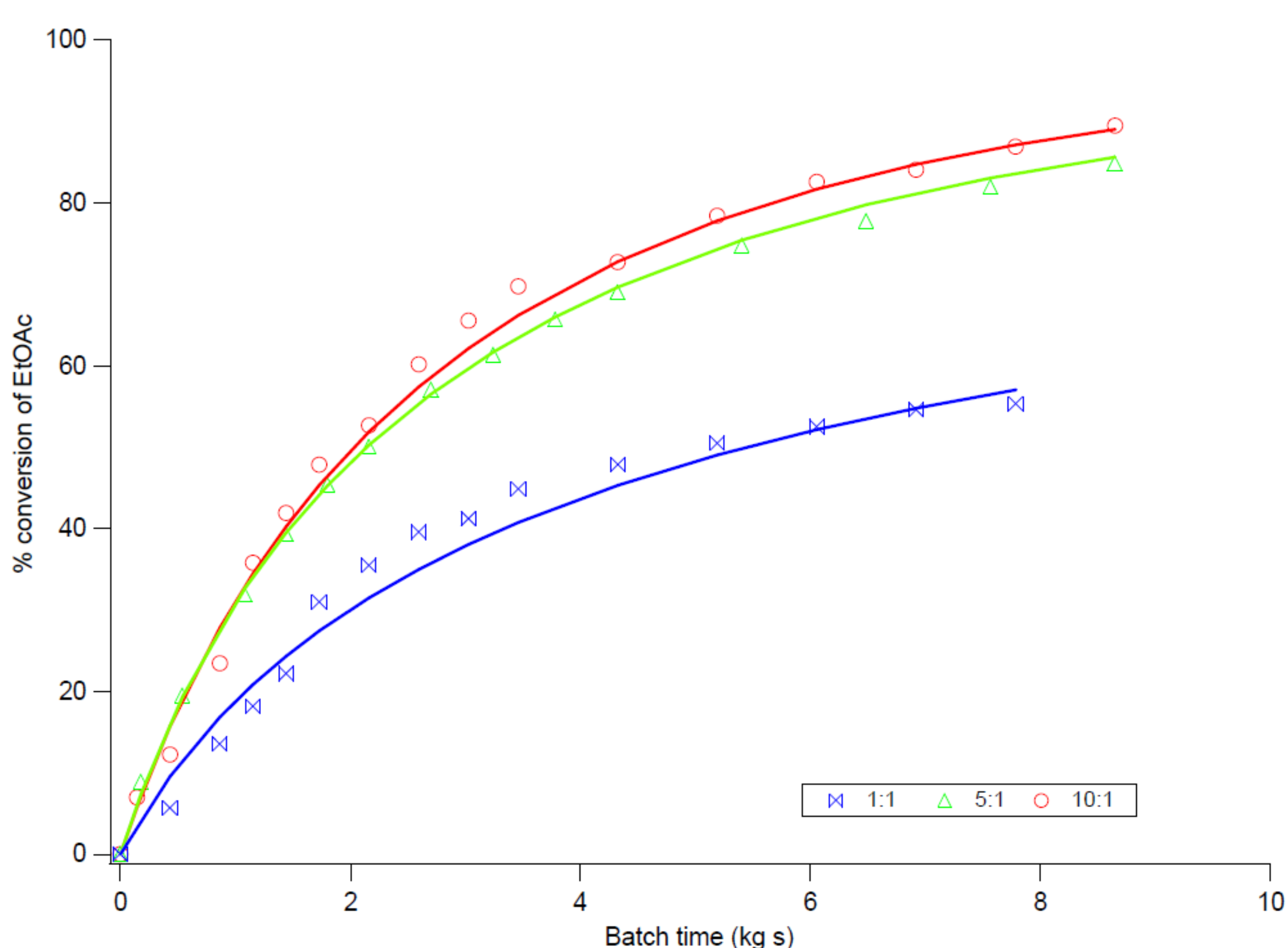


✓ Micropores

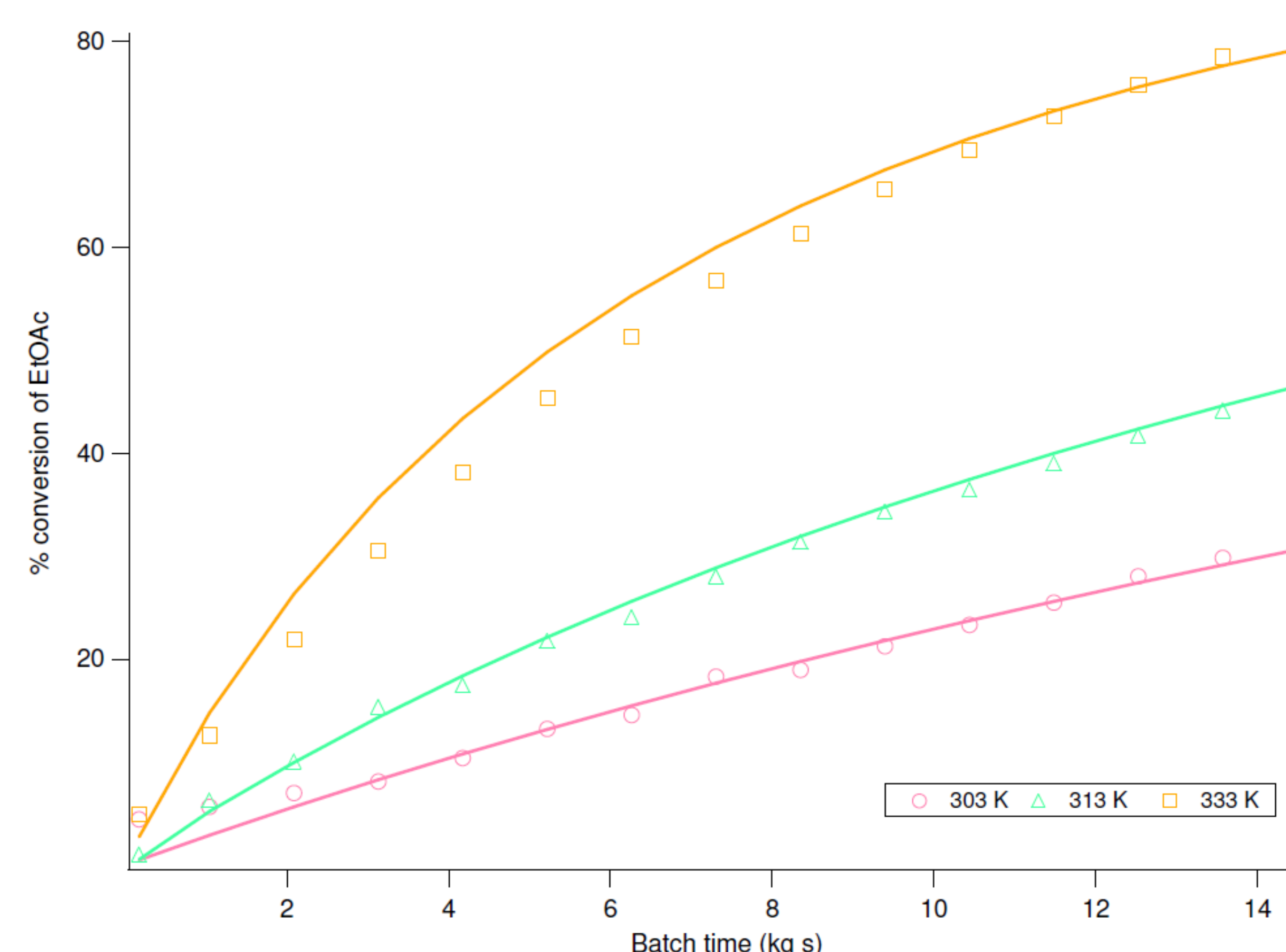
✓ 4 % DVB



## Modelling results



$k_{SR} (10^{-3} \text{ mol kg}_{cat}^{-1} \text{ s}^{-1})$	
$50.8 \pm 6.0$	$52.7 \pm 0.3$
$E_A (kJ \text{ mol}^{-1})$	
$46.1 \pm 1.9$	$48.7 \pm 0.9$
$K_r$	
$4.3 \pm 0.3$	$1.2 \pm 0.1$
$K_p$	
$0.0$	$4.9 \pm 0.4$
$K_w$	
$7.9 \pm 0.7$	



## Conclusions & perspectives

- ✓ Temperature and initial molar ratio effect adequately modelled with proposed reaction mechanism.
- ✓ In the mechanism are **all the acid sites covered** and is **sorption** expressed by an **exchange**.
- ✓ **Activation energy of 48 kJ mol<sup>-1</sup>**, irrespective of the reaction type.
- ✓ **Unique set of exchange coefficients** for each reaction.
- ✓ **High value** of ion-exchange coefficient  $K_w$  shows the **inhibiting** effect of water on the esterification.
- ✓ For 333 K and initial molar ratio of 10:1, at **least 60 %** of the catalyst's **active sites** were covered by **methanol**

## Acknowledgements